

# Dynamic contact angle of a liquid spreading on an unsaturated wettable porous substrate

Shikhmurzaev, Yulii; Sprittles, James

DOI:  
[10.1017/jfm.2012.517](https://doi.org/10.1017/jfm.2012.517)

*Document Version*  
Publisher's PDF, also known as Version of record

*Citation for published version (Harvard):*  
Shikhmurzaev, Y & Sprittles, J 2013, 'Dynamic contact angle of a liquid spreading on an unsaturated wettable porous substrate', *Journal of Fluid Mechanics*, vol. 715, pp. 273-282. <https://doi.org/10.1017/jfm.2012.517>

[Link to publication on Research at Birmingham portal](#)

## General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

## Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.

# Dynamic contact angle of a liquid spreading on an unsaturated wettable porous substrate

Yulii D. Shikhmurzaev<sup>†</sup> and James E. Sprittles

School of Mathematics, University of Birmingham, Birmingham B15 2TT, UK  
Mathematical Institute, University of Oxford, Oxford OX1 3LB, UK

(Received 3 April 2012; revised 10 August 2012; accepted 15 October 2012)

The spreading of an incompressible viscous liquid over an isotropic homogeneous unsaturated porous substrate is considered. It is shown that, unlike the dynamic wetting of an impermeable solid substrate, where the dynamic contact angle has to be specified as a boundary condition in terms of the wetting velocity and other flow characteristics, the ‘effective’ dynamic contact angle on an unsaturated porous substrate is completely determined by the requirement of existence of a solution, i.e. the absence of a non-integrable singularity in the spreading fluid’s pressure at the ‘effective’ contact line. The obtained velocity dependence of the ‘effective’ contact angle determines the critical point at which a transition to a different flow regime takes place, where the fluid above the substrate stops spreading whereas the wetting front inside it continues to propagate.

**Key words:** contact lines, interfacial flows (free surface), porous media

---

## 1. Introduction

The modelling of the spreading of liquids over porous substrates in the framework of continuum mechanics requires, and is based on, the separation of scales between the ‘macroscopic’ (or ‘Darcy scale’) and ‘microscopic’ (or ‘pore-scale’) processes (Barenblatt, Entov & Ryzhik 1990). In the continuum approximation, the description of the spreading phenomenon brings in the notion of an ‘effective’ smooth penetrable solid substrate, which is how the actual porous medium is represented, together with the notions of ‘effective’ contact lines and ‘effective’ contact angles that the free surface of the pure fluid above and the wetting front inside the substrate form with it. These notions, being averages in the sense of mechanics of multiphase media (Whitaker 1999), are fundamentally different from the concepts of ‘contact line’ and ‘contact angle’ used in the modelling of dynamic wetting on the actual, as opposed to ‘effective’, impermeable solid surfaces. In particular, the notion of a ‘static’ (or ‘equilibrium’) contact angle, central to the modelling of dynamic wetting where it is a measure of wettability of the solid (Ralston, Popescu & Sedev 2008), becomes meaningless for the Darcy-scale description of the liquid spreading over a porous medium: as experiments show (e.g. Clarke *et al.* 2002; Starov *et al.* 2003; Markicevic, D’Onofrio & Navaz 2010), if, say, a drop of liquid is deposited onto an unsaturated

<sup>†</sup> Email address for correspondence: [yulii@for.mat.bham.ac.uk](mailto:yulii@for.mat.bham.ac.uk)

wettable porous substrate, the eventual equilibrium state will be the drop completely imbibed into the porous medium, with no liquid left above it and hence no ‘effective’ static (equilibrium) contact angle between the, now non-existent, free surface of the pure liquid and the effective surface of the substrate.

The main theoretical implication of this absence of a meaningful effective static (equilibrium) contact angle is that the effective *dynamic* contact angle that the free surface of a spreading liquid forms with a porous substrate on the Darcy scale cannot be regarded as essentially a perturbation of the static contact angle, which is what one invariably finds in all models dealing with the dynamic wetting of impermeable solid surfaces (see Dussan V. 1979; de Gennes 1985; Blake 2006; Shikhmurzaev 2011, for reviews). Therefore, it becomes important to consider the problem from first principles, without implying *a priori* that the case of a porous substrate can be described by adjusting the concepts borrowed from the modelling of dynamic wetting of impermeable solid surfaces, such as the equilibrium contact angle.

In the present paper, we show that, unlike the situation one has in dynamic wetting, where the ‘microscopic’ dynamic contact angle has to be specified as an additional boundary condition, for the process of the fluid spreading over a porous substrate one can find the ‘effective’ dynamic contact angle from the requirement of the absence of a non-integrable singularity of the fluid’s pressure at the contact line, i.e. essentially from the requirement that a solution exists. The limits confining the considered regime suggest certain experimentally verifiable predictions of the model which we briefly discuss in the light of the available experimental data.

(As a clarifying remark, it is necessary to point out that the ‘microscopic’ dynamic contact angle in the dynamic wetting situation referred to in the previous paragraph should not be confused with the so-called ‘apparent’ contact angle resulting from the free surface bending near the contact line. Unlike the ‘microscopic’ angle which has to be specified, this ‘apparent’ angle is not part of the mathematical problem formulation; it is an auxiliary concept introduced, in some works and in different ways (see e.g. Wilson *et al.* 2006), to interpret experimental results when the measured angle differs from the (‘microscopic’) angle imposed in the problem formulation. It is also worth mentioning here that, in what follows, the flow inside the porous matrix is treated in the standard way, i.e. employing a dynamic wetting model for the impermeable solid surface to describe the propagation of menisci in the pores.)

## 2. Problem formulation

Consider an incompressible Newtonian fluid of density  $\rho$  and viscosity  $\mu$  spreading at a speed  $U$  over an isotropic homogeneous unsaturated porous substrate characterized by an effective pore size  $a$ . The gas displaced by the fluid from the substrate and from the inside of the porous matrix is assumed to be ideal and at a constant pressure with respect to which the pressure in the pure fluid and in the fluid inside the porous medium will be measured. In order to be able to model the process in the framework of continuum mechanics, we need a separation of scales between the macroscopic and the pore-scale phenomena, i.e. we have to consider the continuum limit

$$\epsilon = \frac{a}{L} \rightarrow 0, \quad (2.1)$$

where  $L$  is the characteristic length scale on which the phenomenon is described. The resulting model will be applicable to experiments if  $a/L \ll 1$ , with the actual value of  $a/L$  determining its accuracy. In the zeroth approximation in the above limit, one has (see figure 1): (a) a macroscopic ‘wetting front’ as a sharp interface  $S_w$  separating the

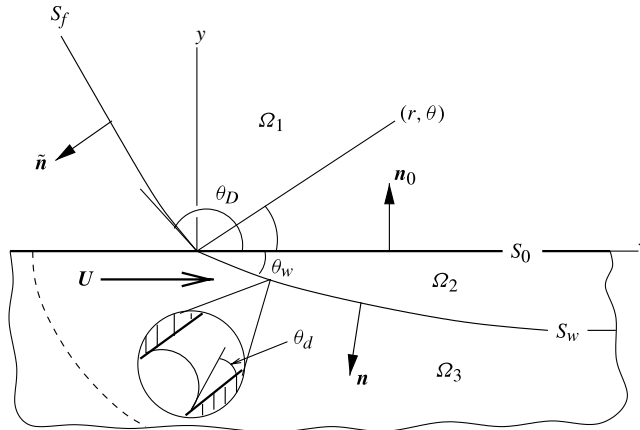


FIGURE 1. Sketch of the spreading of a viscous liquid over an unsaturated wettable porous substrate in a coordinate frame moving with the contact line in the framework of continuum mechanics. The magnified view illustrates the main flow mode on the pore scale, where  $\theta_d$  is the dynamic contact angle formed by the moving meniscus with the wall of the pore. Regions  $\Omega_1$ ,  $\Omega_2$  and  $\Omega_3$  correspond to the pure liquid, the saturated part of the porous medium and the unsaturated porous matrix, respectively;  $\theta_D$  is the ‘effective’ dynamic contact angle formed by the free surface of the liquid  $S_f$  with the surface  $S_0$  of the ‘effective’ porous substrate, and  $S_w$  is the wetting front inside the substrate.

saturated porous medium  $\Omega_2$  from the unsaturated matrix  $\Omega_3$ ; (b) an effective ‘contact line’ at which the free surface  $S_f$ , confining the domain  $\Omega_1$  occupied by the pure fluid, and the wetting front meet; and (c) well-defined ‘contact angles’  $\theta_D$  and  $\theta_w$  that the free surface and the wetting front form with the ‘effective’ surface  $S_0$  of the solid. The reference frame in which the problem will be considered and the directions of unit normals  $\mathbf{n}$ ,  $\tilde{\mathbf{n}}$  and  $\mathbf{n}_0$  to, respectively,  $S_w$ ,  $S_f$  and  $S_0$  are shown in the figure. Importantly, in the scheme outlined above we have already made an assumption that the two contact lines, i.e. the contact line CL1 formed with the substrate by the free surface  $S_f$  and the contact line CL2 formed with it by the wetting front  $S_w$ , coincide. This is always what happens when the fluid is first brought in contact with the substrate, for example, when a liquid drop impinges upon a porous solid and starts to spread. We will examine what follows from this combination of forced spreading and imbibition behind the front of the spreading liquid. Then, we will consider the conditions when the assumption that CL1 and CL2 coincide no longer holds and the two contact lines separate.

We will consider the case of small Reynolds and capillary numbers for the flow of the pure fluid, i.e. the limit  $Re = \rho LU / \mu \rightarrow 0$  and

$$Ca = \frac{\mu U}{\sigma} \rightarrow 0, \quad (2.2)$$

where  $\sigma$  is the surface tension of the fluid–gas interface. In this limit, to leading order, inertial effects can be neglected, and, as in the case of the dynamic wetting of an impermeable solid surface (Huh & Scriven 1971; Shikhmurzaev 1993), from the normal-stress boundary condition on the free surface we have that near the contact line the free surface ( $S_f$ ) is locally planar, so that locally  $\Omega_1$  is a wedge region. For

simplicity we will also neglect gravity, though its inclusion would not change the main results of the analysis below.

Scaling the pressure and velocity in  $\Omega_1$  with  $\mu U/L$  and  $U$  respectively, one has that in  $\Omega_1$  the dimensionless pressure  $\tilde{p}$  and velocity  $\tilde{\mathbf{u}}$  obey the Stokes equations

$$\nabla \cdot \tilde{\mathbf{u}} = 0, \quad \nabla \tilde{p} = \nabla^2 \tilde{\mathbf{u}} \quad (\mathbf{r} \in \Omega_1), \quad (2.3)$$

and on the free surface satisfy the standard kinematic and tangential-stress boundary conditions,

$$\tilde{\mathbf{u}} \cdot \tilde{\mathbf{n}} = 0, \quad \tilde{\mathbf{n}} \cdot [\nabla \tilde{\mathbf{u}} + (\nabla \tilde{\mathbf{u}})^T] \cdot (\mathbf{I} - \tilde{\mathbf{n}}\tilde{\mathbf{n}}) = 0 \quad (\mathbf{r} \in S_f), \quad (2.4)$$

where  $\mathbf{I}$  is the metric tensor.

In the porous medium, the flow is driven by the capillary pressure in the menisci that collectively form the wetting front, and, for the problem in question, the characteristic pressure and velocity are  $2\sigma/a$  and  $U$ , respectively. Using the notation  $p$  and  $\mathbf{u}$  for the dimensionless pressure and velocity in  $\Omega_2$ , in a frame moving with the contact line we have an equation of motion in the form of Darcy's law,

$$\mathbf{u} - \hat{\mathbf{U}} = -K\nabla p \quad (\mathbf{r} \in \Omega_2), \quad (2.5)$$

where  $K = 2\sigma\kappa/(\mu aLU)$  is the non-dimensionalized permittivity of the porous matrix ( $\kappa$  is the actual permittivity) and  $\hat{\mathbf{U}} = \mathbf{U}/U$  is a unit vector directed along the velocity of the porous substrate. Given that in porous media  $\kappa \propto a^2$  (Probstein 1989), we have that  $K = O(\epsilon/Ca)$  and, for the problem to be non-trivial, it is assumed to be finite in the limits (2.1), (2.2). In the present context, it is convenient to define  $L$  by setting  $K = 1$ .

Since the porosity  $\phi$  in a homogeneous matrix is constant, the mass balance equation has the standard form  $\nabla \cdot \mathbf{u} = 0$ , so that, after substituting (2.5) into it, one arrives at Laplace's equation for  $p$  in  $\Omega_2$ :

$$\nabla^2 p = 0 \quad (\mathbf{r} \in \Omega_2). \quad (2.6)$$

On the wetting front, one has the kinematic condition that the front propagates with the velocity of the fluid, i.e. in the reference frame described above where the process is steady,

$$\mathbf{u} \cdot \mathbf{n} = 0 \quad (\mathbf{r} \in S_w), \quad (2.7)$$

and needs to specify the dynamic condition on the pressure  $p$ . To formulate this condition in a general case, one has to consider the modes of motion the menisci go through on the pore scale as the macroscopic wetting front propagates (Shikhmurzaev & Sprittles 2012a,b). Here we will be considering the simplest case involving the main, 'wetting', mode. In this case, for an 'effective' pore with a circular cross-section the dimensionless pressure at the front is given by

$$p = -\cos \theta_d, \quad (2.8)$$

where  $\theta_d$  is the contact angle formed on the pore scale by the representative meniscus with the pore wall (figure 1). Unlike the simplified approach pioneered by Washburn (1921), where it is assumed that  $\theta_d$  is constant and equal to the prescribed static contact angle  $\theta_s$ , we need to take into account that, as demonstrated by numerous experiments (e.g. see Shikhmurzaev 2007, Ch. 3 for a review),  $\theta_d$  depends on the wetting speed, i.e. to consider the dependence

$$(\mathbf{u} - \hat{\mathbf{U}}) \cdot \mathbf{n} = U_{cl}^* f(\theta_d) \quad (\mathbf{r} \in S_w), \quad (2.9)$$

where  $U_{cl}^*$  is the appropriate velocity scale depending on the material parameters of the system (as for all velocities above, we have non-dimensionalized it using  $U$ ). The function  $f(\theta_d)$  has to be determined theoretically or empirically. For example, one can apply  $f(\theta_d)$  derived using the theory of dynamic wetting as a process of interface formation (Shikhmurzaev 2007), which has been shown to reliably describe experimental data, though, in the present context, any function  $f(\theta_d)$  representing the experimentally observed dependence of the form (2.9) could be used, such as, for instance, the one that comes from the molecular-kinetic theory of wetting (Blake & Haynes 1969). For more information about the dynamic wetting modelling we refer the reader to a recent review (Shikhmurzaev 2011).

From the theory of flows with forming interfaces one has

$$\left. \begin{aligned} f(\theta_d) &= \left( \frac{(1 + (1 - \rho_{1e}^s) \cos \theta_s) (\cos \theta_s - \cos \theta_d)^2}{4(\cos \theta_s + B)(\cos \theta_d + B)} \right)^{1/2}, \\ U_{cl}^* &\equiv \frac{U_{cl}}{U} = \frac{1}{U} \left( \frac{\gamma \rho_{(0)}^s (1 + 4\alpha\beta)}{\tau\beta} \right)^{1/2}, \end{aligned} \right\} \quad (2.10)$$

where

$$B = (1 - \rho_{1e}^s)^{-1} (1 + \rho_{1e}^s u_0(\theta_d)), \quad u_0(\theta_d) = \frac{\sin \theta_d - \theta_d \cos \theta_d}{\sin \theta_d \cos \theta_d - \theta_d}, \quad (2.11)$$

and  $\rho_{(0)}^s$ ,  $\rho_{1e}^s$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\tau$  are material constants characterizing the contacting media. Their values for some systems can be found elsewhere (Blake & Shikhmurzaev 2002; Shikhmurzaev 2007).

So far, the flow in the pure fluid and in the porous medium have been considered separately, and to link them one has to specify three boundary conditions at  $S_0$ . One condition that we obviously have on this surface is the continuity of mass flux:

$$(\tilde{\mathbf{u}} - \phi \mathbf{u}) \cdot \mathbf{n}_0 = 0 \quad (\mathbf{r} \in S_0). \quad (2.12)$$

For the velocity components parallel to  $S_0$ , i.e. for  $\tilde{\mathbf{u}}_{\parallel} \equiv \tilde{\mathbf{u}} \cdot (\mathbf{I} - \mathbf{n}_0 \mathbf{n}_0)$  and  $\mathbf{u}_{\parallel} \equiv \mathbf{u} \cdot (\mathbf{I} - \mathbf{n}_0 \mathbf{n}_0)$ , a number of boundary conditions have been discussed in the literature (e.g. Saffman 1971; Jones 1973; Murdoch & Soliman 1999; Nield 2009; Auriault 2010), following the experiments reported by Beavers & Joseph (1967) and an empirical condition these authors proposed. As noted, for example, by Auriault (2010), these conditions are aimed at capturing the effects of  $O(\epsilon)$ , i.e. go beyond the classical, i.e. zeroth-order, approximation in the continuum limit (2.1). In the zeroth approximation, all these conditions reduce to no-slip for the pure fluid,

$$\tilde{\mathbf{u}}_{\parallel} = \hat{\mathbf{U}}_{\parallel} \quad (\mathbf{r} \in S_0), \quad (2.13)$$

and it is this condition that we will be using here.

The condition of continuity of pressure on  $S_0$  in the dimensionless form yields that

$$p = \tilde{p} \frac{\epsilon Ca}{2}, \quad (2.14)$$

and hence, to leading order in the limits (2.1) and (2.2), one has

$$p = 0 \quad (\mathbf{r} \in S_0). \quad (2.15)$$

Importantly, unlike the case of an impermeable solid substrate, where one has to specify the dynamic contact angle (as we need to specify  $\theta_d$  on the pore scale), here,

for the effective contact angle  $\theta_D$ , we will require only that the flow parameters in the porous medium remain regular at the contact line and that the solution in the pure fluid exists.

### 3. Dynamic contact angle

Consider the asymptotic behaviour of the solution to (2.3)–(2.15) in the case of a two-dimensional flow as the distance to the contact line  $r \rightarrow 0$ . In the polar coordinates  $(r, \theta)$  shown in figure 1, to leading order, for the pressure  $p$  in the porous medium one has

$$\frac{\partial^2 p}{\partial r^2} + \frac{1}{r} \frac{\partial p}{\partial r} + \frac{1}{r^2} \frac{\partial^2 p}{\partial \theta^2} = 0, \quad (-\theta_w < \theta < 0), \quad (3.1)$$

$$p(r, 0) = 0 \quad \frac{\partial p}{\partial \theta}(r, -\theta_w) = r \sin \theta_w, \quad (3.2)$$

where the last condition follows from (2.7) and (2.5). The separable solution to this problem is obviously given by

$$p = r \tan \theta_w \sin \theta, \quad (3.3)$$

so that, using the dynamic boundary condition (2.8), we obtain that

$$\theta_d = \arccos(-r \tan \theta_w \sin \theta_w) \rightarrow \frac{\pi}{2} \quad \text{as } r \rightarrow 0. \quad (3.4)$$

Then, from (2.9), where now  $(\mathbf{u} - \hat{\mathbf{U}}) \cdot \mathbf{n} = \sin \theta_w$ , we have an equation determining  $\theta_w$ :

$$\sin \theta_w = U_{cl}^* f(\pi/2). \quad (3.5)$$

In order to consider the flow in the pure fluid, we introduce a stream function

$$\tilde{u}_r = \frac{1}{r} \frac{\partial \tilde{\psi}}{\partial \theta}, \quad \tilde{u}_\theta = -\frac{\partial \tilde{\psi}}{\partial r}, \quad (3.6)$$

so that for the leading-order term  $\tilde{\psi}_1$  of the asymptotic expansion of  $\tilde{\psi}$  as  $r \rightarrow 0$  we have a biharmonic equation

$$\left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right)^2 \tilde{\psi}_1 = 0 \quad (0 < r, 0 < \theta < \theta_D), \quad (3.7)$$

together with conditions (2.4), i.e.

$$\tilde{\psi}_1(r, \theta_D) = 0, \quad \frac{\partial^2 \tilde{\psi}_1}{\partial \theta^2}(r, \theta_D) = 0, \quad (3.8)$$

on the free surface, and conditions (2.12) and (2.13), i.e.

$$\tilde{\psi}_1(r, 0) = r \phi \tan \theta_w, \quad \frac{\partial \tilde{\psi}_1}{\partial \theta}(r, 0) = r, \quad (3.9)$$

on the surface of the solid substrate. In writing down the first of conditions (3.9) we made use of (3.3) and integrated along  $S_0$ .

The separable solution to the problem (3.7)–(3.9) has the form

$$\tilde{\psi}_1 = r(A_1 \sin \theta + A_2 \theta \sin \theta + A_3 \cos \theta + A_4 \theta \cos \theta), \quad (3.10)$$

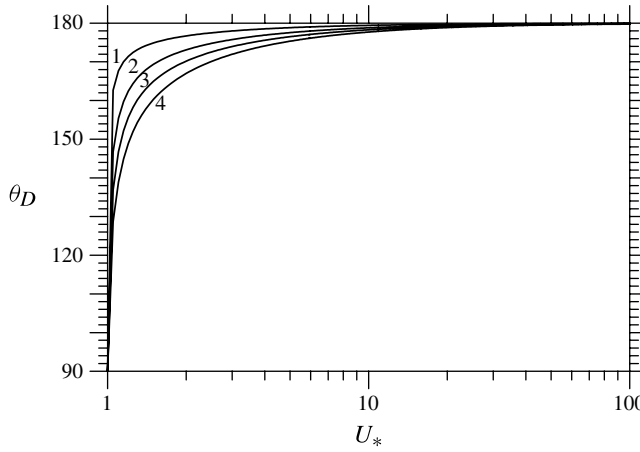


FIGURE 2. Dependence of the effective dynamic contact angle  $\theta_D$  on the dimensionless contact-line speed  $U_*$  for different porosities. Curves 1, 2, 3 and 4 correspond to  $\phi = 0.1, 0.2, 0.3$  and  $0.4$ , respectively.

where the constants  $A_1, \dots, A_4$  are given by

$$A_1 = -\frac{\theta_D}{\sin \theta_D \cos \theta_D - \theta_D} - A_3 \frac{\cos^2 \theta_D}{\sin \theta_D \cos \theta_D - \theta_D}, \quad (3.11)$$

$$A_2 = \frac{\sin^2 \theta_D}{\sin \theta_D \cos \theta_D - \theta_D} + A_3 \frac{\sin \theta_D \cos \theta_D}{\sin \theta_D \cos \theta_D - \theta_D}, \quad (3.12)$$

$$A_3 = \phi \tan \theta_w, \quad A_4 = A_2 \cot \theta_D. \quad (3.13)$$

Using (3.6), we can write down the radial projection of the second equation in (2.3) in the form

$$\frac{\partial \tilde{p}}{\partial r} = \left( \frac{1}{r} \frac{\partial^3}{\partial r^2 \partial \theta} + \frac{1}{r^3} \frac{\partial^3}{\partial \theta^3} + \frac{1}{r^2} \frac{\partial^2}{\partial r \partial \theta} \right) \tilde{\psi}_1, \quad (3.14)$$

and, after substituting the solution (3.10), arrive at

$$\frac{\partial \tilde{p}}{\partial r} = -\frac{2}{r^2} (\sin \theta + \cot \theta_D \cos \theta) A_2. \quad (3.15)$$

Thus, the leading term in the coordinate expansion of the stream function will not give rise to a non-integrable singularity of pressure if and only if  $A_2 = 0$ , or, using (3.12) and (3.13),

$$\tan \theta_D = -\phi \tan \theta_w. \quad (3.16)$$

Given the expression (3.5) for  $\sin \theta_w$  and introducing the dimensionless contact-line speed  $U_* \equiv 1/(f(\pi/2)U_{cl}^*) = U/(f(\pi/2)U_{cl})$ , we can also write this equation as

$$\theta_D = \pi + \arctan \left( -\frac{\phi}{\sqrt{U_*^2 - 1}} \right). \quad (3.17)$$

This equation specifies  $\theta_D$  in terms of the speed  $U$  of the contact line with respect to the substrate, the porosity of the matrix  $\phi$  and the material properties of the contacting media accumulated in  $U_{cl}$  and  $f(\pi/2)$ . The velocity-dependence of  $\theta_D$  for different porosities is shown in figure 2. As one can see, this dependence is much steeper than



the velocity-dependence of the dynamic contact angle for the dynamic wetting of an impermeable substrate (e.g. see Shikhmurzaev 2007, Ch. 3 for a review). In particular,  $d\theta_D/dU_* \rightarrow +\infty$  as  $U_* \rightarrow 1+$ .

The dynamic contact angle given by (3.17) ensures integrability of the normal stress on the free surface and hence the existence of a solution. The next term in the asymptotic expansion of  $\tilde{\psi}$  has the form  $\tilde{\psi}_2 = r^2 F(\theta)$  and therefore can give rise, at most, to a logarithmic (i.e. integrable) singularity of  $\tilde{p}$  at the contact line, which does not affect the existence of the solution.

The obtained result has a clear physical meaning. In the case we are considering, the dynamics of imbibition determines the normal to the substrate component of the pure fluid's velocity independently of the pure fluid's bulk flow, and, given that the tangential component of the fluid's velocity on the surface of the substrate is prescribed, as it satisfies the no-slip condition with a known speed of the substrate, we have a moving contact-line problem where on the solid surface both components of velocity are set. In this situation, in the pure fluid the solution exists only if from the family of stream functions described by (3.10) we choose the one that corresponds to a uniform flow ( $A_2 = 0$ ,  $A_4 = 0$ ) with the projections of velocity on the normal and tangential to the substrate directions equal to the speed of imbibition and the speed of the solid substrate, respectively.

The solution (3.17) for steady spreading of a fluid over an unsaturated substrate ceases to exist when the dimensionless velocity  $U_*$  becomes equal to 1 and both  $\theta_D$  and  $\theta_w$  reach  $\pi/2$ . For  $U_* < 1$  we have a different regime with the two contact lines CL1 and CL2 no longer coinciding as the wetting front moves ahead (dashed line in figure 1), and the pure fluid finds itself on a saturated substrate. Then, in the vicinity of CL1 the pressure  $p$  satisfies Laplace's equation  $\nabla^2 p = 0$  together with the boundary conditions

$$p(r, 0) = 0, \quad \frac{\partial p}{\partial \theta}(r, -\pi) = 0, \quad (3.18)$$

and the local solution with the regular pressure gradient has the form

$$p = \sum_{n=1}^{\infty} C_n r^{1/2+n} \sin\left(\frac{1}{2} + n\right) \theta, \quad (3.19)$$

where  $C_n$ ,  $n = 1, 2, \dots$  are constants. Then, according to (2.5) and (2.12), one has  $\tilde{u}_\theta(r, 0) \propto r^{1/2} \rightarrow 0$  as  $r \rightarrow 0$ . As a result, if  $\tilde{u}_r(r, 0) = O(1)$  as  $r \rightarrow 0$ , then, to leading order as  $r \rightarrow 0$ , we will have the 'classical' moving contact-line problem, with no imbibition and the no-slip boundary condition on the solid. This problem, as is well known (see e.g. Shikhmurzaev 2007, Ch. 3), has no solution. The only way out of this situation is to conclude that, as CL1 and CL2 separate, the contact line CL1 stops moving. Then, for the pure fluid one simply has a static contact line with the imbibition velocity  $\propto r^{1/2}$  near it and  $\theta_D = \pi/2$ . It is easy to verify that the solution to this problem exists. As CL1 and CL2 separate and CL2 moves ahead, the imbibition process near CL1 slows down, leading to  $C_1 = 0$  in (3.19) and hence  $\tilde{u}_\theta \propto r^{3/2}$ , so that  $\theta_D$  no longer has to be equal to  $\pi/2$  and can decrease as the imbibition continues.

#### 4. Discussion

The described scenario is in agreement with the available experimental data. In experiments on spreading drops, it has been observed that the regime where the drop base and the saturated area underneath it expand together is followed by the regime

where the two contact lines, CL1 and CL2, separate, as drop's base stops expanding whereas the saturated area continues to grow (Clarke *et al.* 2002; Starov *et al.* 2003; Keshav & Basu 2007; Markicevic *et al.* 2010). This is usually attributed to the 'competition' between spreading and imbibition, and the above analysis shows what this actually means.

Markicevic *et al.* (2010) report that in their experiment the spreading droplet maintained the shape of a spherical cap throughout the process and that its base stopped expanding when 'the droplet is a half of sphere'. In other words, it stopped expanding when the dynamic contact angle  $\theta_D$  became equal to  $90^\circ$ . This is exactly what follows from the result of our analysis.

The dependence of the effective contact angle  $\theta_D$  on the contact-line speed for  $U_* > 1$  given by (3.17) and illustrated in figure 2 awaits experimental verification. The issue here is that, to extract this dependence from experiments with unsteady flows, one has to deal with very short time intervals ( $\ll 40$  ms according to Markicevic *et al.* 2010) with a well-controlled spatial resolution and conditions of the Darcy-scale description satisfied. The problem is made more complicated by the fact that, as one can see in figure 2, the velocity-dependence of  $\theta_D$  is very steep, which brings in additional conditions on the temporal resolution of the experiments. On the other hand, experiments with steady flows of the kind commonly used to study dynamic wetting of an impermeable solid surface require sizeable substrates with well-reproducible properties. To date, no systematic measurements of  $\theta_D$  with controlled spatial resolution have been reported.

As we have shown, the requirement of the absence of a non-integrable singularity of pressure in the pure fluid at the contact line, which is equivalent to the requirement of the existence of a solution, uniquely specifies the velocity-dependence of the 'effective' dynamic contact angle  $\theta_D$  formed by the free surface and the 'effective' surface of the porous substrate. In practical computations, it may be convenient to set (3.17) as a boundary condition while considering the normal-stress condition on the free surface as the equation determining the free surface shape. One implication of the obtained result is that, if one specifies  $\theta_D$  as an additional boundary condition different from (3.17), then, for a solution to exist, it will become necessary to use a slip boundary condition instead of the no-slip condition (2.13) employed here (Davis & Hocking 2000). As mentioned earlier, this would mean bringing effects of  $O(\epsilon)$  into the essentially classical, i.e.  $O(1)$  as  $\epsilon \rightarrow 0$ , formulation. If a velocity-dependence of  $\theta_D$  different from (3.17) is imposed together with the no-slip condition (2.13) for the pure fluid (Alleborn & Raszillier 2004; Reis, Griffiths & Santos 2004), then there will be no solution to the problem, although this fact can be hidden behind, and as a result masked by, simplifying assumptions made in the process of finding the solution (e.g. lubrication approximation) and the numerical implementation.

From the theoretical viewpoint, it would be interesting to consider the essentially unsteady process of separation of CL1 and CL2, which marks the transition between the two regimes described above. As with every finite-time transition, this is a challenging problem deserving a detailed investigation.

#### REFERENCES

- ALLEBORN, N. & RASZILLIER, H. 2004 Spreading and sorption of a droplet on a porous substrate. *Chem. Engng Sci.* **59**, 2071–2088.
- AURIAULT, J.-L. 2010 About the Beavers and Joseph boundary condition. *Transp. Porous Med.* **83**, 257–266.

- BARENBLATT, G. I., ENTOV, V. M. & RYZHIK, V. M. 1990 *Theory of Fluid Flows through Natural Rocks*. Kluwer.
- BEAVERS, G. S. & JOSEPH, D. D. 1967 Boundary conditions at a naturally permeable wall. *J. Fluid Mech.* **30**, 197–207.
- BLAKE, T. D. 2006 The physics of moving wetting lines. *J. Colloid Interface Sci.* **299**, 1–13.
- BLAKE, T. D. & HAYNES, J. M. 1969 Kinetics of liquid/liquid displacement. *J. Colloid Interface Sci.* **30**, 421–423.
- BLAKE, T. D. & SHIKHMURZAEV, Y. D. 2002 Dynamic wetting by liquids of different viscosity. *J. Colloid Interface Sci.* **253**, 196–202.
- CLARKE, A., BLAKE, T. D., CARRUTHERS, K. & WOODWARD, A. 2002 Spreading and imbibition of liquid droplets on porous surfaces. *Langmuir* **18**, 2980–2984.
- DAVIS, S. H. & HOCKING, L. M. 2000 Spreading and imbibition of viscous liquid on a porous base. II. *Phys. Fluids* **12**, 1646–1655.
- DUSSAN V., E. B. 1979 On the spreading of liquids on solid surfaces: static and dynamic contact lines. *Annu. Rev. Fluid Mech.* **11**, 371–400.
- DE GENNES, P.-G. 1985 Wetting: statics and dynamics. *Rev. Mod. Phys.* **57**, 827–863.
- HUH, C. & SCRIVEN, L. E. 1971 Hydrodynamic model of steady movement of a solid/liquid/fluid contact line. *J. Colloid Interface Sci.* **35**, 85–101.
- JONES, I. P. 1973 Low Reynolds number flow past a porous spherical shell. *Proc. Camb. Phil. Soc.* **73**, 231–238.
- KESHAV, T. R. & BASU, S. 2007 Spreading of liquid droplets on proton exchange membrane of a direct alcohol fuel cell. *Chem. Engng Sci.* **62**, 7515–7522.
- MARKICEVIC, B., D'ONOFRIO, T. G. & NAVAZ, H. K. 2010 On spread extent of sessile droplet into porous medium: numerical solution and comparison with experiments. *Phys. Fluids* **22**, 012103.
- MURDOCH, A. I. & SOLIMAN, A. 1999 On the slip boundary condition for liquid flow over planar porous boundaries. *Proc. R. Soc. Lond. A* **455**, 1315–1340.
- NIELD, D. A. 2009 The Beavers–Joseph boundary condition and related matters: a historical and critical note. *Transp. Porous Med.* **78**, 537–540.
- PROBSTEN, R. F. 1989 *Physicochemical Hydrodynamics: An Introduction*. Butterworth.
- RALSTON, J., POPESCU, M. & SEDEV, R. 2008 Dynamics of wetting from an experimental point of view. *Annu. Rev. Mater. Res.* **38**, 23–43.
- REIS, N. C. JR., GRIFFITHS, R. F. & SANTOS, J. M. 2004 Numerical simulation of the impact of liquid droplets on porous surfaces. *J. Comput. Phys.* **198**, 747–770.
- SAFFMAN, P. G. 1971 On the boundary condition at the surface of a porous medium. *Stud. Appl. Maths* **50**, 93–101.
- SHIKHMURZAEV, Y. D. 1993 The moving contact line on a smooth solid surface. *Intl J. Multiphase Flow* **19**, 589–610.
- SHIKHMURZAEV, Y. D. 2007 *Capillary Flows with Forming Interfaces*. Chapman & Hall/CRC.
- SHIKHMURZAEV, Y. D. 2011 Some dry facts about dynamic wetting. *Eur. Phys. J.* **197**, 47–60 (special topics).
- SHIKHMURZAEV, Y. D. & SPRITTLES, J. E. 2012a Anomalous dynamics of capillary rise in porous media. *Phys. Rev. E* **86**, 016306.
- SHIKHMURZAEV, Y. D. & SPRITTLES, J. E. 2012b Wetting front dynamics in an isotropic porous medium. *J. Fluid Mech.* **694**, 399–407.
- STAROV, V. M., ZHDANOV, S. A., KOSVINTSEV, S. R., SOBOLEV, V. D. & VELARDE, M. G. 2003 Spreading of liquid drops over porous substrates. *Adv. Colloid Interface Sci.* **104**, 123–158.
- WASHBURN, E. W. 1921 The dynamics of capillary flow. *Phys. Rev.* **17**, 273–283.
- WHITAKER, S. 1999 *The Method of Volume Averaging*. Kluwer.
- WILSON, M. C. T., SUMMERS, J. L., SHIKHMURZAEV, Y. D., CLARKE, A. & BLAKE, T. D. 2006 Non-local hydrodynamic influence on the dynamic contact angle: slip models versus experiment. *Phys. Rev. E* **73**, 041606.